

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

B3

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B22F 9/24, 1/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/24576</b> <b>(43) International Publication Date:</b> 11 June 1998 (11.06.98)
<b>(21) International Application Number:</b> PCT/US97/22614 <b>(22) International Filing Date:</b> 4 December 1997 (04.12.97)  <b>(30) Priority Data:</b> 60/032,112 5 December 1996 (05.12.96) US  <b>(71) Applicant:</b> THE UNIVERSITY OF CONNECTICUT [US/US]; 438 Whitney Road, Storrs, CT 06268 (US).  <b>(72) Inventors:</b> XIAO, Tongsan, D.; Apartment 99, 70 Pinney Hill Road, West Willington, CT 06279 (US). STRUTT, Peter, R.; 126 Clover Mill Road, Mansfield Center, CT 06250 (US). TORBAN, Steve; 4355 Fushia Circle, South Palm Beach Gardens, FL 33410 (US).  <b>(74) Agent:</b> REIMER, Leah, M.; Fishman, Dionne, Cantor & Colburn, 88 Day Hill Road, Windsor, CT 06095 (US).		<b>(81) Designated States:</b> CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> NANOSTRUCTURED METALS, METAL ALLOYS, METAL CARBIDES AND METAL ALLOY CARBIDES AND CHEMICAL SYNTHESIS THEREOF		
<b>(57) Abstract</b> <p>A new chemical method for the synthesis of nanostructured metal, metal alloys, metal carbides, and metal alloy carbides, such as nickel, chromium, cobalt, iron, molybdenum, tungsten, and vanadium, nickel/chromium, iron/titanium, iron/nickel, tungsten/cobalt, iron/chromium/molybdenum, and nickel chromium carbide and iron titanium carbide is presented. The method involves reductive decomposition of an organic solution of at least one metal precursor using sodium triethyl borohydride. Preferably, the reducing agent is introduced by means of atomization. After co-precipitation of a nanoscale metal or metal alloy powder, low temperature annealing is used to form nanostructured crystalline powders, or low temperature gas phase carburization to form nanostructured Ni-Cr<sub>3</sub>C<sub>2</sub> cermet powder.</p>		
<p style="text-align: right;"><b>BEST AVAILABLE COPY</b></p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## NANOSTRUCTURED METALS, METAL ALLOYS, METAL CARBIDES AND METAL ALLOY CARBIDES AND CHEMICAL SYNTHESIS THEREOF

### Background of the Invention

#### 1. Field of the Invention

This invention relates to methods for the synthesis of nanostructured metals, metal alloys, and metal carbides. In particular, this invention relates to chemical methods for the synthesis of nanostructured metals, metal alloys and ceramic/metal composites of controlled morphology. The obtained materials exhibit superior properties, including improved fracture toughness, hardness, and wear-, corrosion-, and erosion-resistance. Some of these materials also possess outstanding catalytic properties.

#### 2. Brief Description of the Prior Art

Materials having fine-scale microstructures, that is grain sizes on the order of a few micrometers (microns) possess unique and technologically attractive properties. Recently, however, research has focused on reducing grain size from the micrometer to the nanometer range. Such nanostructured materials have diameters in the range of about 2 to about 100 nm (1 nm = 10 angstroms), or on the order of molecular dimensions. A feature of nanostructured materials is the high fraction of atoms (up to

-2-

50%) that reside at grain or particle boundaries. It is often possible to design unique features and properties at the atomic level into such materials by subtle manipulation of the reaction environment. One feature of particular interest is pore structure and packing density of nanophase materials at the atomic level. Nanostructured materials often have superior chemical and physical properties in comparison to conventional counterparts having the same chemical composition.

Thus, considerable advantages accrue from the substitution of nanostructured materials for conventional microstructured materials in a wide variety of applications. These include superior strength, wear resistance, and fracture toughness in martensitic steel; the reduced sintering temperature for powder consolidation and the onset of superplasticity in nanostructured ceramics; improved ductility in ceramic/metal composites (cermets); and reduced thermal conductivity for thermal barrier coatings.

Nanostructured metals, metal alloys and metal carbides in particular are expected to have improved fracture toughness, as well as improved resistance to wear, corrosion, and erosion (see, for example, the examples set forth in Nanostructured Materials, Volume 1, 1992. Such materials also have potential as advanced catalysts. Certain nickel/chromium (Ni/Cr) alloys, for example, have high strength, excellent hot corrosion resistance and superior wear properties, making them attractive candidate materials for a wide range of high temperature applications, for example, as wear resistant coatings in the hot sections of gas turbine and diesel engines.

Nickel/chromium carbide (Ni-Cr<sub>x</sub>C<sub>y</sub>) alloys are also of interest. At low chromium (Cr) concentrations, Ni/Cr alloys are fcc substitutional solid solutions ( $\gamma$ -phase). At higher chromium concentrations which exceed the solubility limit in nickel (Ni), the equilibrium structure is a two-phase mixture of fcc Ni/Cr solid solution ( $\gamma$ -phase) and bcc chromium ( $\alpha$ -phase). The corresponding chromium carbide-rich alloys contain a variety of carbide phases: Cr<sub>23</sub>C<sub>6</sub>, Cr<sub>6</sub>C, Cr<sub>2</sub>C or Cr<sub>3</sub>C<sub>2</sub>. Alloys of commercial interest have a high volume fraction of Cr<sub>3</sub>C<sub>2</sub> carbide (typically greater than about 60 mole %) dispersed in a Ni/Cr solid solution.

Nanostructured Ni/Cr and Ni-Cr<sub>3</sub>C<sub>2</sub> alloys have not been reported. Microstructured Ni/Cr and Ni-Cr<sub>3</sub>C<sub>2</sub> alloys, however, have produced by melting and

-3-

casting methods. Rapid solidification processing technologies, including powder atomization and melt spinning, have more recently achieved finer and more homogeneous structures. However, in order to produce materials with ultrafine or nanoscale structures, alternative processing routes are required. Accordingly, there remains a need in the art for a chemical synthetic method for the production of nanostructured metals, metal alloys, and metal carbides.

#### Summary of the Invention:

The above-discussed and other drawbacks and deficiencies of the prior art are overcome or alleviated by the chemical synthetic method of the present invention for the production of nanostructured metals, metal alloys and metal carbides, including metals such as nickel, chromium, cobalt, iron, molybdenum, tungsten, and vanadium, metal alloys such as nickel/chromium, iron/titanium, iron/nickel, tungsten/cobalt, iron/chromium/molybdenum, and metal carbides such as nickel chromium carbide, nickel titanium carbide, molybdenum titanium carbide and iron titanium carbide. In accordance with the present invention, a starting solution is provided comprising metal salts in a suitable solvent. Optionally, the composition of the starting solution may be adjusted to yield a variety of metal alloy nanostructured powders, thus allowing tailoring of the chemical, structural and performance characteristics of the final powders. A reducing agent is then added to the solution. Preferably, the reducing agent is atomized into the starting solution via a pressurized nozzle, allowing precise control of the nucleation and growth of the nanostructured metal or metal alloy powder. The as-synthesized metal or metal alloy powder is isolated by filtration and washed, passivated with deoxygenated mineral oil, and stored under inert gas. The powder may be heat treated in a high-temperature, environmentally controlled furnace.

In another embodiment of the present invention, the above nanostructured metal or metal alloy powder is reacted with a carbon source using gas phase carburization techniques. After carburization, the obtained powder is dispersed in distilled, deoxygenated water to remove by-products from the nanostructured cermet powder.

The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings.

#### Brief Description of the Drawings

5 Referring now to the drawings wherein like elements are numbered alike in the several FIGURES:

FIGURE 1 is XRD patterns for nanostructured, crystalline Ni/Cr alloys of different compositions after heat treatment (all at 600 °C, except for the 80 mole % Ni/Cr alloy, which was heat treated at 700 °C.)

10 FIGURE 2 is a graph showing particle size of the nanostructured nickel ( $\gamma$ -phase) and chromium ( $\alpha$ -phase) as a function of alloy composition.

FIGURE 3 is (a) a bright-field TEM micrograph and (b) corresponding electron diffraction pattern of the nanostructured 20 mole % nickel in Ni/Cr alloy.

15 FIGURE 4 is a histogram showing particle size distribution of the 20 mole % nickel in Ni/Cr alloy obtained by computer image analysis of the TEM micrograph of FIGURE 3(a).

FIGURE 5 is XRD patterns showing the effect of heat treatment on an 80 mole % nickel in Ni/Cr alloy powder.

20 FIGURE 6 is XRD patterns showing the effect of heat treatment on an 20 mole % nickel in Ni/Cr alloy powder.

FIGURE 7 is a prior art equilibrium phase diagram of the Ni/Cr alloy system.

FIGURE 8 is a graph comparing the lattice parameters of the nanocrystalline alloys of the present invention with the prior art data lattice parameters of Ni/Cr alloys.

25 FIGURE 9 is an XRD pattern of the nanocrystalline 20 mole % Ni-Cr<sub>3</sub>C<sub>2</sub> composite powder.

FIGURE 10 is (a) a bright-field TEM micrograph and (b) corresponding electron diffraction pattern of the 20 mole % Ni-Cr<sub>3</sub>C<sub>2</sub> composite powder.

-5-

FIGURE 11 is a histogram showing particle size distribution obtained from computer image processing of the TEM micrograph of the 20 mole % Ni-Cr<sub>3</sub>C<sub>2</sub> composite powder.

#### Detailed Description of the Invention

5           As will be explained in more detail below, nanostructured metals and metal alloys are synthesized in accordance with the present invention by first providing a starting solution comprising at least one metal salt in a suitable solvent. Optionally, the composition of the starting solution may be adjusted by addition of additional metal precursors to yield a variety of nanostructured metal alloy powders, thus allowing  
10 tailoring of the chemical, structural and performance characteristics of the final powders. A reducing agent is then added to the starting solution, preferably by atomization via a pressurized nozzle, allowing precise control of the nucleation and growth of the nanophase powder. A nanostructured powder is formed, and the as-synthesized powder is washed and filtered, passivated with deoxygenated mineral  
15 oil, and stored under inert gas. The powder may be heat treated in a high-temperature, environmentally controlled furnace.

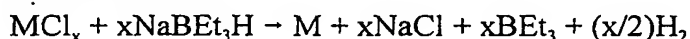
In the first step of the method a starting solution is provided, prepared from at least one metal salt and a solvent such as toluene, methanol, and/or water. Suitable  
20 metal salts are those which will yield the desired metal or metal alloy upon reduction, including but not limited to chlorides and nitrate of transition metals, for example, Ni, Cr, and other transition metals such as Co, V, W, Fe, Mo, Mn, Cu, Ti, and the like.

Where required, the compositions of the starting solutions are adjusted to yield a range of nanostructured metal alloy powders, with tailored chemical, structural, and performance characteristics. The adjustment includes but is not limited to the addition  
25 of a soluble salt of the second, third or greater metal, or the addition of acid or base to the starting solution. Suitable alloying metals include but are not limited to metals, transition metals such as Ni, Cr, Co, V, W, Fe, Mo, Mn, Cu, Ti, and the like, and semiconductor metals known in the art.

-6-

A reducing agent is then introduced into the starting solution or adjusted starting solution. The process is preferably carried out by atomizing the reducing agent into the metal salt solution via a pressurized nozzle or ultrasound, or adding the solution dropwise into the metal salt solution. Thus, the nucleation and growth of the nanophase powder can be precisely and reproducibly controlled. Suitable reducing agents include lithium or sodium triethylborohydride, or lithium or sodium borohydride. Alternatively, the metal salt may be atomized into a solution of reducing agent.

The reduction of metal halides to form metal clusters, for example, is represented by the following equation:



where  $\text{M} = \text{Ni}$  for  $x = 2$  and  $\text{M} = \text{Cr}$  for  $x = 3$ . According to previous studies on the reduction of similar metal halides, this reaction either may result from direct hydride transfer to form a metal hydride intermediate, which subsequently reductively eliminates hydrogen, or occurs directly by an electron-transfer mechanism. Metal halides may also be reduced by sodium borohydride to form nanostructured metals and metal alloys. In this instance, however, reactions are carried out in an aqueous medium instead of an organic solvent.

The next step comprises isolation and washing of the nanostructured suspensions using deoxygenated water or other solvents. The high surface area reactive powder is then passivated with deoxygenated mineral oil and stored under an inert gas. Where appropriate, the powder may be heat treated in a high-temperature environmentally-controlled furnace.

Some high surface area metal powders obtained from this reduction process are extremely air and moisture sensitive such as nickel-based alloys. Initial experiments to purify nanostructured nickel metal powders from by-products such as NaCl used extensive washing with deoxygenated water, which was followed by the application of a protective coating of deoxygenated mineral oil. XRD analysis of the washed powders indicated that the powders were highly disordered or amorphous, since only very broad nickel and chromium peaks were observed. Attempts to convert the powders into

-7-

crystalline form via high temperature heat treatment resulted in the formation of a greenish powder, which consisted of nickel and  $\text{Cr}_2\text{O}_3$  phases. During the course of the heat treatment it was observed that once the furnace temperature reached 60 °C, a sudden temperature increase up to 300 °C occurred over a few minutes, even though the heating rate was only set at a few degrees per minute. Based on these observations and analytical results, it is hypothesized that the O-H groups of water molecules are initially physisorbed into the metal surface. Upon slow heating, these O-H groups are gradually transformed into chemisorbed species, which then react with the metal powders to form  $\text{Cr}_2\text{O}_3$ , instead of being evaporated away in the heat treatment process.

To avoid this oxidation problem, the air and moisture sensitive precipitated powders are coated with deoxygenated mineral oil before washing. In this case, C-H groups derived from the mineral oil and residual toluene are first physisorbed onto the metal surfaces. These physisorbed C-H groups gradually transform into chemisorbed species during heat treatment, and then react with the metal surfaces to form thin layers of protective carbide phase. Since these layers are extremely thin, they are not detectable by XRD analysis. However, ICP analysis indicates that there is appreciable carbon content in such sample. Importantly, the initial heating rate during heat treatment of these materials should be extremely slow below 300 °C. Otherwise, the C-H groups will be partially evaporated, and this will create problems of slow burning of the sample upon exposure to air after treatment. Thus, it appears that the transformation of the physisorbed C-H groups into chemisorbed species is very important for passivation of certain metals and alloys, such as Ni/Cr alloys.

To obtain nanostructured metal/ceramic composites, the obtained metal or metal alloys are reacted with a carbon source using gas phase carburization. Such gas phase carburization is well-known in the art. After carburization, the powder is dispersed in distilled oxygenated water to remove by-products from the nanostructured cermet powder.

Examples of the materials which may be synthesized by the above methods include nanostructured transition metals, for example nickel, chromium, and other transition metals such as Co, V, W, Fe, Mo, and the like, nanostructured transition

-8-

metal alloys such as Ni/Cr, Fe/Ti, Fe/Ni, W/Co, Fe/Cr/Mo, and the like, as well as nanostructured nickel chromium carbide and nanostructured iron titanium carbide.

The invention will be further illustrated by the following non-limiting examples.

### EXAMPLES

5           Nickel chloride ( $\text{NiCl}_2$ ), chromium chloride ( $\text{CrCl}_3$ ) and a 1.0 M toluene solution of sodium triethylborohydride ( $\text{NaBEt}_3\text{H}$ ) were obtained from Aldrich Chemical, Inc., Milwaukee, WI. The toluene solvent was first dried over calcium chloride, refluxed, distilled, and then deoxygenated. All manipulations were carried out under an atmosphere of ultrahigh purity nitrogen (99.99% purity) using standard  
10       Schlenk techniques, because of the oxygen and moisture sensitivities of the starting compounds and the resulting nanostructured powders.

The nanostructured Ni/Cr alloy and  $\text{Ni-Cr}_3\text{C}_2$  powders were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and inductively coupled plasma spectroscopy (ICP).

#### 15       Example 1: Nanostructured Ni/Cr

Nanostructured Ni/Cr powders were prepared with the following compositions: 100% Ni, 80 mole % Ni in Ni/Cr, 50 mole % Ni in Ni/Cr, 20 mole % Ni in Ni/Cr and 100 % Cr. In a typical experiment, e.g., for 20 mole % Ni in Ni/Cr, 16.43 gm of  $\text{CrCl}_3$   
20       (0.1038 mol) and 3.36 gm of  $\text{NiCl}_2$  (0.0259 mol) were dispersed in 400 mL of deoxygenated toluene to form a purple suspension in a 2-liter, 3-neck flask equipped with a magnetic stirrer and gas inlet/outlet tubes. A stream of  $\text{N}_2$  was bubbled through the stirred solution for 2 hours at room temperature, then the 400 mL of a 1.0 M toluene solution of  $\text{NaBEt}_3\text{H}$  was also slowly added dropwise into the halide mixture via a pressure equalized addition funnel at temperature under a nitrogen atmosphere. A black  
25       suspension slowly formed while hydrogen gas evolved. The suspension was stirred for 48 hours at room temperature to ensure complete reduction of the halides. The black powder was filtered and washed with deoxygenated toluene under a stream of nitrogen. At this stage, no attempt was made to remove the sodium chloride byproduct. The high

surface area reactive powder was passivated with deoxygenated mineral oil and stored in a Schlenk flask under nitrogen. Other compositions of the nanostructured Ni-Cr powders were prepared in a similar manner.

In variation to the above dropwise addition, the 400 mL of a 1.0 M toluene solution of  $\text{NaBEt}_3\text{H}$  was atomized to the halide mixture via a pressurized nozzle under a nitrogen atmosphere. In this approach, the nucleation and growth of the nanostructured powder can be precisely controlled.

Heat treatment was performed using a high temperature, environmentally controlled Lindburg tube furnace. About 2 grams of the powder mixture was placed in an alumina boat inside an alumina tube having an inner diameter 32 mm. Prior to heat treatment, the chamber was evacuated to about  $10^{-5}$  torr ( $1.33 \times 10^{-3}$  Pa), flushed with argon repeatedly, and backfilled with argon to near ambient pressure. Heat treatment was carried out at 300-600 °C with a fume gas (97% Ar, 3%  $\text{H}_2$ ) flow rate of about 1 L/min. The sample was first slowly heated to 300 °C in 1.5 hours, and then heated to the desired peak temperature at a heating rate of 25 °C/min, with a dwell time at the heat treatment temperature of 1 hour. After heat treatment, the fine powder was suspended in distilled water and then centrifuged to separate the sodium chloride and water from the nanostructured Ni/Cr alloy powder.

FIGURE 1 is XRD patterns of the nanostructured, crystalline Ni/Cr alloy powders of different compositions after heat treatment at 600 °C. Where chromium concentration is below 50 mole %, only nickel is detected, and the peaks correspond to fcc Ni/Cr. Where chromium concentrations are greater than 50 mole %, both nickel and chromium are detected, and the nickel peaks correspond to fcc Ni/Cr, and the chromium peaks to bcc chromium. Values of the lattice constants for Ni/Cr and chromium are listed in the Table below. The lattice parameter of the nanostructured, crystalline nickel powder is estimated to be  $a = 3.5264 \text{ \AA}$ , which agrees well with the known bulk value for nickel ( $a = 3.5238 \text{ \AA}$ ). With increasing chromium concentration from 20 to 80 mole %, the lattice parameter gradually increases:  $a = 3.5437 \text{ \AA}$  for 20% Cr,  $a = 3.5457 \text{ \AA}$  for 50% Cr, and  $3.5513 \text{ \AA}$  for 80% Cr. The lattice parameter of the nanostructured, crystalline chromium powder is determined to be  $a = 2.8854 \text{ \AA}$ , which again is in good

-10-

agreement with the known bulk value for pure chromium ( $a = 2.8839 \text{ \AA}$ ). As the concentration of nickel increases from 0 to 50 mole %, there is a slight increase of the Cr lattice parameter:  $a = 2.8908 \text{ \AA}$  for 20% Ni, and  $a = 2.8957 \text{ \AA}$  for 50% Ni.

Composition	Ni lattice Parameter	Cr lattice Parameter
100% Ni	3.5264 $\text{\AA}$	---
20% Cr	3.5437 $\text{\AA}$	---
50% Cr	3.5457 $\text{\AA}$	2.8957 $\text{\AA}$
80% Cr	3.5513 $\text{\AA}$	2.8908 $\text{\AA}$
100% Cr	---	2.8854 $\text{\AA}$

The crystallite size of the nanostructured powder was determined from x-ray peak broadening. FIGURE 2 shows the variation in particle size of nanostructured, crystalline Ni/Cr alloy as a function of chromium concentration. The particle size of Ni/Cr ( $\gamma$ -phase) varied from 10 nm to 18 nm, being about 10 nm for 100 mole % Ni, 13 nm for 80 mole % Ni in Ni/Cr, 10 nm for 50 mole % Ni in Ni/Cr, and 18 nm for 20 mole % Ni in Ni/Cr. The particle size of chromium ( $\alpha$ -phase) is also shown in FIGURE 2. The particle sizes of the  $\alpha$ -phase chromium were determined to be 14 nm for 100 mole % Cr, 29 nm for 80 mole % Cr, and 21 nm for 50 mole % Cr.

A typical TEM micrograph for a 20 mole % Ni in Ni/Cr alloy powder is shown in FIGURE 3 and a particle size distribution as determined by image analysis was performed (see FIGURE 4). The average particle size of the nanocrystalline alloy was 12 nm. Selected area diffraction of the powders showed the presence of fcc nickel and bcc chromium.

The effects of heat treatment on the crystallinity and phase formation of the nanostructured powders was also investigated. FIGURE 5 shows XRD results for the 80 mole % nickel in Ni/Cr alloy. The as-synthesized Ni/Cr powder is amorphous. The 300 °C heat treated sample is also amorphous. At 400 °C, the XRD peaks for nickel start to appear, superimposed on a very diffuse background intensity. As the annealing

temperature increases, the diffraction peaks sharpen and the diffuse background decreases. At 500 °C and 600 °C, there is an observable background intensity in combination with very well-defined nickel crystalline peaks. At 700 °C, there is no diffuse background and the nickel phase peaks are sharp; but no chromium phase is detected in this particular composition. The crystallite size of the nickel phase increases from 4 nm to 13 nm when the temperature is increased from 300 °C to 600 °C, and is about 20 nm at 700 °C. At lower annealing temperatures, for example, below 600 °C other broad peaks are also evident. At 400 °C, two very broad peaks are centered at about  $2\theta = 37^\circ$  and  $62^\circ$ . Relative intensities of these two peaks decrease as the annealing temperature increases, and they finally disappear at a temperature of 700 °C.

FIGURE 6 shows XRD results for heat treatment of 20 mole % Ni in Ni/Cr. Once again, the as-synthesized powder is amorphous. After heat treatment at 300 °C, only nickel peaks are detected. At higher temperatures, however, peaks for both nickel and chromium phases are observed. At 500 °C, no amorphous background is observed, but there is phase separation of nickel and chromium. At this temperature, the XRD signal of the nickel phase is strong, but the XRD signal of the chromium phase is weak. After heat treatment at 600 °C, well-defined XRD peaks of the chromium phase are visible. The crystallite size of the nickel phase increases from 4 nm to 20 nm when the annealing temperature increases from 300 °C to 600 °C, while the chromium phase increases from 2 nm to 15 nm when the temperature increases from 500 °C to 600 °C.

The alloy powders are extremely fine after heat treatment and they can be readily dispersed in a solvent. Even after several months of storage, they show no evidence of settling. After washing in distilled water, they could not be separated from NaCl and water because all of the particles passed through the microporous filter. The separation process, however, may be accomplished by agglomerating the nanoparticles into micron-size agglomerates by centrifugation followed by filtering. Morphological examination of these agglomerates by SEM shows that they are several tens of microns in size. From all of the above results, it is concluded that the powders after centrifugal processing are micron size agglomerates consisting of an assemblage of nanostructured,

crystalline Ni/Cr alloy particles. The agglomerates can be easily broken down into their individual entities via ultrasonic agitation.

The established Ni-Cr phase diagram is shown in FIGURE 7. At a composition of less than 36 mole % Cr only  $\gamma$ -phase is at the Ni-rich region, where chromium atoms are substitutional. The  $\alpha$ -phase is at the chromium-rich region, where only a very small amount ( $< 2\%$ ) of nickel solute atoms are substitutional. In the nanostructured, crystalline Ni-Cr system, only fcc nickel XRD signals were detected (see FIGURE 1) at 100 mole % Ni and 20 mole % Cr, with an increased lattice parameter for the 20 mole % chromium sample. This data is in agreement with the established phase diagram for conventional micron-sized Ni/Cr, since these compositions are at the single phase field ( $\gamma$ -phase). At higher concentrations of chromium, for example, 50 mole % Cr and 80 mole % Cr, both  $\gamma$ -phase and  $\alpha$ -phase were evident, as predicted by the phase diagram. This data illustrates that the experimental findings for the nanostructured, crystalline Ni-Cr system agree very well with the established phase diagram for the conventional microstructured, crystalline Ni-Cr system.

FIGURE 8 is a comparison of the lattice parameters for conventional microstructured, crystalline Ni/Cr alloys as described in Floyd and Taylor, J. Inst. Met., Vol. 80, pp. 169 (1952) and the corresponding nanostructured, crystalline Ni/Cr alloys. In the experiments of Floyd and Taylor, the alloys of various compositions were heat treated at 1100 °C for six days. The samples were then cooled by either (i) rapid quenching to room temperature, or (ii) slow cooling to room temperature by furnace cooling. The lattice parameter vs. composition plots for both sets of samples had a similar slope up to 45 mole % chromium, which is indicative of the presence of only one phase, the  $\gamma$ -phase. For the present nanostructured Ni/Cr alloys, it was found that at low concentrations of chromium, for example, 0% Cr and 20 mole % Cr, the measured lattice parameters agreed well with the data obtained by Floyd and Taylor. However, a slope change was evident at higher concentrations of chromium. It may be that the nanostructured alloy has already reached its solubility limit around of 29 mole % chromium at a temperature of 600 °C. Upon increasing the concentration of chromium, phase separation into  $\gamma$ - and  $\alpha$ -phases occurs.

Example 2: Ni-Cr<sub>3</sub>C<sub>2</sub> Powders

Nanostructured Ni-Cr<sub>3</sub>C<sub>2</sub> powder can be prepared by the gas phase carburization technique described by L.E. McCandlish, B.H. Kear and B.K. Kim, in Nanostruct. Mater. Vol. 1, p. 119 (1992) by high temperature fluidized bed reactor at near ambient pressure, herein incorporated by reference in its entirety. However, the process described herein use a vacuum carburization technique, which is routinely used in commercial carburization of steels.

About 2 grams of the nanostructured 80 mole %Cr/20 mole %Ni powder was transferred into a tubular carburization unit equipped with vacuum pumps, pressure gauges, and inlet/outlet gas tubes. The carburization unit was first evacuated to about 5 m torr, flushed with argon, and backfilled with methane to 200 torr. Carburization was accomplished at a temperature of 880 °C and a pressure of 200 torr. The heating rate and the dwell time at the reaction temperature was 60 °C/min and 1 hour, respectively. After carburization, the powder was dispersed in distilled water and then centrifuged to remove sodium chloride and water from the nanophase cermet powder. As shown by the XRD analysis (FIGURE 9) this alloy composition resulted in the formation of a nanostructured mixture of nickel and Cr<sub>3</sub>C<sub>2</sub>.

Morphological examination using SEM reveals that the cermet powder has a porous structure, but detailed information can not be obtained due to the very small particle size. A typical TEM micrograph of the powder is shown in FIGURE 10(a), which reveals a size distribution of particles ranging from a few nanometers to several tens of nanometers. Particle size analysis from the bright field micrograph via an image processing technique, FIGURE 11, indicates that the average particle size of the Ni-Cr<sub>3</sub>C<sub>2</sub> powder is about 34 nm. Using x-ray line broadening analysis, particle size of the nickel phase is shown to be 18 nm, and that of the Cr<sub>3</sub>C<sub>2</sub> phase is 30 nm. This discrepancy in particle size may be attributed to overlapping particles not being taken into consideration in the image analysis technique, and the presence of amorphous regions in the particle grain boundaries. Electron diffraction analysis confirmed the presence of nickel and Cr<sub>3</sub>C<sub>2</sub> phases. The individual particle sizes of the two different phases could not be determined from the phase contrast in the TEM studies.

-14-

In summary, a new chemical method for the synthesis of nanostructured Ni/Cr and Ni-Cr<sub>3</sub>C<sub>2</sub> alloys is presented. The method involves reductive decomposition of an organic solution of metal chloride precursors using sodium triethyl borohydride. After co-precipitation of amorphous nanostructured mixed metal (Ni+Cr) powder, low  
5 temperature annealing is used to form nanostructured, crystalline Ni/Cr alloy powder, or low temperature gas phase carburization to form nanostructured, crystalline NiCr<sub>3</sub>C<sub>2</sub> cermet powder.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit  
10 and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

What is claimed is:

---

-15-

CLAIM 1. A nanostructured metal, metal alloy, metal carbide or metal alloy carbide powder comprising:

5 nanostructured chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, vanadium, or a combination thereof, wherein the particles of the metal, metal alloy, or metal carbide have diameters of less than about 100 nanometers.

CLAIM 2. The nanostructured metal, metal alloy, metal carbide or metal alloy carbide powder of claim 1 wherein:

5 the nanostructured metal is chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, or vanadium, the nanostructured metal alloy is nickel/chromium, iron/titanium, iron/nickel, tungsten/cobalt, or iron/chromium/molybdenum, and the nanostructured metal alloy carbide is nickel chromium carbide, cobalt tungsten carbide, nickel titanium carbide, molybdenum titanium carbide, or iron titanium carbide .

CLAIM 3. The nanostructured metal, metal alloy, metal carbide or metal alloy carbide powder of claim 1 wherein:

5 the nanostructured metal is nickel or chromium, the nanostructured metal alloy carbide is nickel/chromium, and the nanostructured metal alloy carbide is nickel/chromium carbide.

CLAIM 4. The nanostructured metal, metal alloy, metal carbide or metal alloy carbide of claim 4 wherein:

the metal or metal alloy is crystalline.

CLAIM 5. A method of synthesizing a nanostructured metal, metal alloy, metal carbide or metal alloy carbide powder, comprising:

providing a starting solution comprising at least one metal salt precursor; and  
treating the starting solution with a reducing agent to form a nanostructured

5 powder precipitate.

-16-

CLAIM 6. The method of claim 5, wherein:

the metal salt precursor is a metal salt of chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, vanadium, or a combination thereof.

CLAIM 7. The method of claim 5, wherein:

the metal salt is a nickel or chromium salt.

CLAIM 8. The method of claim 5, wherein:

the reducing agent is an alkali metal borohydride or an alkali metal alkyl borohydride.

CLAIM 9. The method of claim 5, wherein:

the nanostructured powder precipitate comprises as at least one of chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, or vanadium.

CLAIM 10. The method of claim 5, wherein:

the nanostructured powder precipitate is chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, or vanadium, nickel/chromium, iron/titanium, iron/nickel, tungsten/cobalt, or iron/chromium/molybdenum.

---

CLAIM 11. The method of claim 5, wherein:

the nanostructured powder precipitate is nickel, chromium, or nickel/chromium.

CLAIM 12. The method of claim 5, further comprising:

heat treating the nanostructured powder precipitate is powder to form a nanostructured crystalline powder.

CLAIM 13. The method of claim 5, further comprising:

carburizing the nanostructured powder precipitate to form a metal carbide or a metal alloy carbide.

-17-

CLAIM 14. The method of claim 5, wherein:

the metal carbide or metal alloy carbide is a chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, or vanadium, nickel/chromium, iron/titanium, iron/nickel, tungsten/cobalt, or iron/chromium/molybdenum carbide.

CLAIM 15. The method of claim 5, wherein:

the metal alloy carbide is nickel/chromium carbide.

CLAIM 16. A nanostructured metal or metal alloy powder, wherein:

the nanostructured metal or metal alloy powder is synthesized by reduction of a solution of at least one metal salt precursor with a reducing agent to produce a nanostructured metal or metal alloy powder.

CLAIM 17. The nanostructured metal or metal alloy of claim 16, wherein:

the at least one metal salt precursor comprises chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, vanadium, or a combination thereof.

CLAIM 18. The nanostructured metal or metal alloy of claim 16, wherein:

the at least one metal precursor is a nickel salt or chromium salt.

---

CLAIM 19. The nanostructured metal or metal alloy of claim 16, wherein:

the reducing agent is an alkali metal borohydride, or an alkali metal alkylborohydride.

CLAIM 20. The nanostructured metal or metal alloy powder of claim 16, wherein:

the metal or metal alloy powder is heat treated to provide a nanostructured crystalline powder.

-18-

CLAIM 21. The nanostructured metal or metal alloy powder of claim 16, wherein:  
the metal or metal alloy powder is chromium, cobalt, iron, molybdenum, nickel,  
titanium, tungsten, or vanadium nickel/chromium, iron/titanium, iron/nickel,  
tungsten/cobalt, or iron/chromium/molybdenum.

CLAIM 22. The nanostructured metal or metal alloy powder of claim 16, wherein:  
the metal or metal alloy is nickel, chromium, or nickel/chromium.

CLAIM 23. A nanostructured metal carbide or metal alloy carbide powder, wherein:  
the nanostructured metal carbide or metal alloy carbide powder is synthesized by  
reduction of a solution of at least one metal precursor with a reducing agent to form a  
nanostructured metal or metal alloy powder precipitate, followed by carburization of the  
powder precipitate.

CLAIM 24. The nanostructured metal carbide or metal alloy carbide powder of claim  
24, wherein:

the at least one metal precursor is selected from the group comprising metal  
precursors of chromium, cobalt, iron, molybdenum, nickel, titanium, tungsten, and  
vanadium.

CLAIM 25. The nanostructured metal carbide or metal alloy carbide powder of claim  
24, wherein:

the at least one metal precursor is a nickel salt or chromium salt.

CLAIM 26. The nanostructured metal carbide powder of claim 24, wherein:

the reducing agent is an alkali metal of a borohydride or an alkali metal alkyl  
borhydride.

-19-

CLAIM 27. The nanostructured metal carbide or metal alloy carbide powder of claim 24, wherein:

the metal alloy carbide powder is nickel/chromium carbide or iron/titanium carbide.

1/11

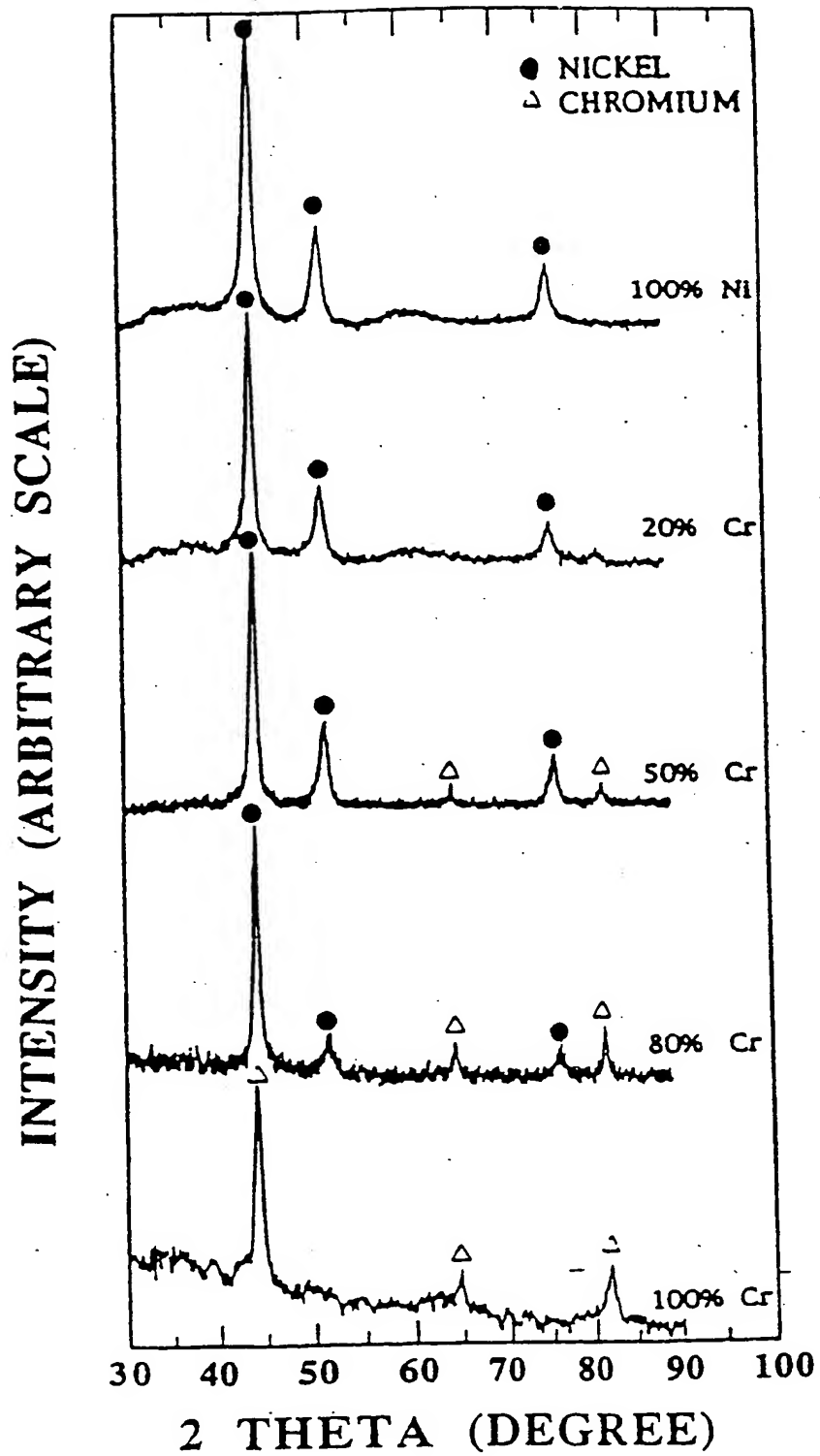


FIGURE 1

2/11

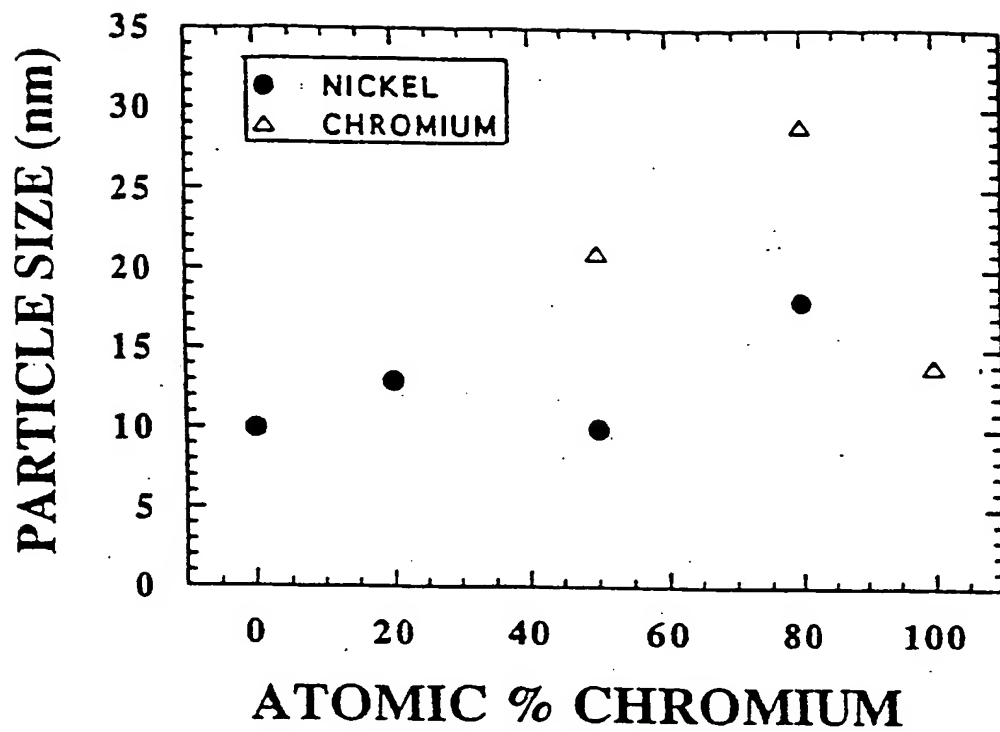


FIGURE 2

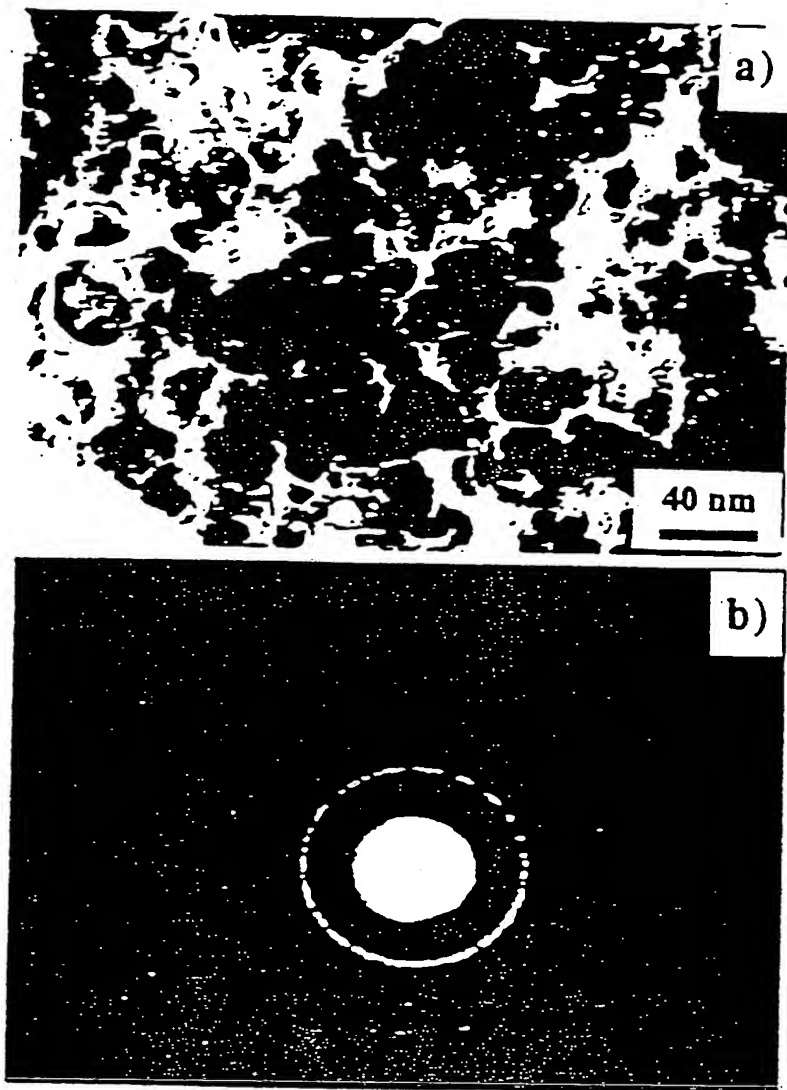


FIGURE 3

4/11

Histogram of Current Image  
Feature : Length  
Unit : nm  
Classes : 20  
Underflow: 0  
Overflow : 0

Frames : 1  
Objects : 434  
Max Cnt : 70  
Min Val : 1.6444  
Max Val : 32.383  
Tot Sum : 5319.9  
Mean : 12.258  
Std Dev : 5.3271

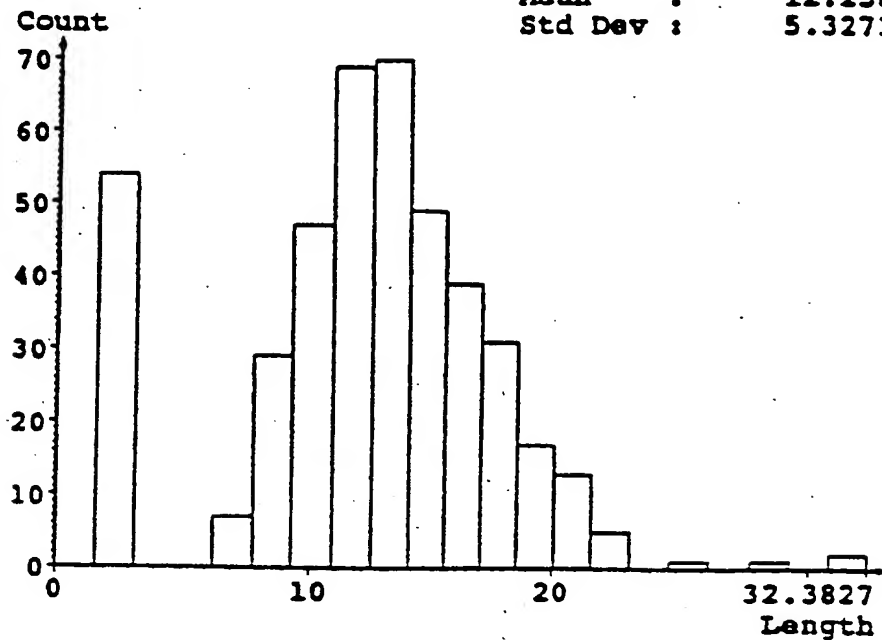


Figure 4

5/11

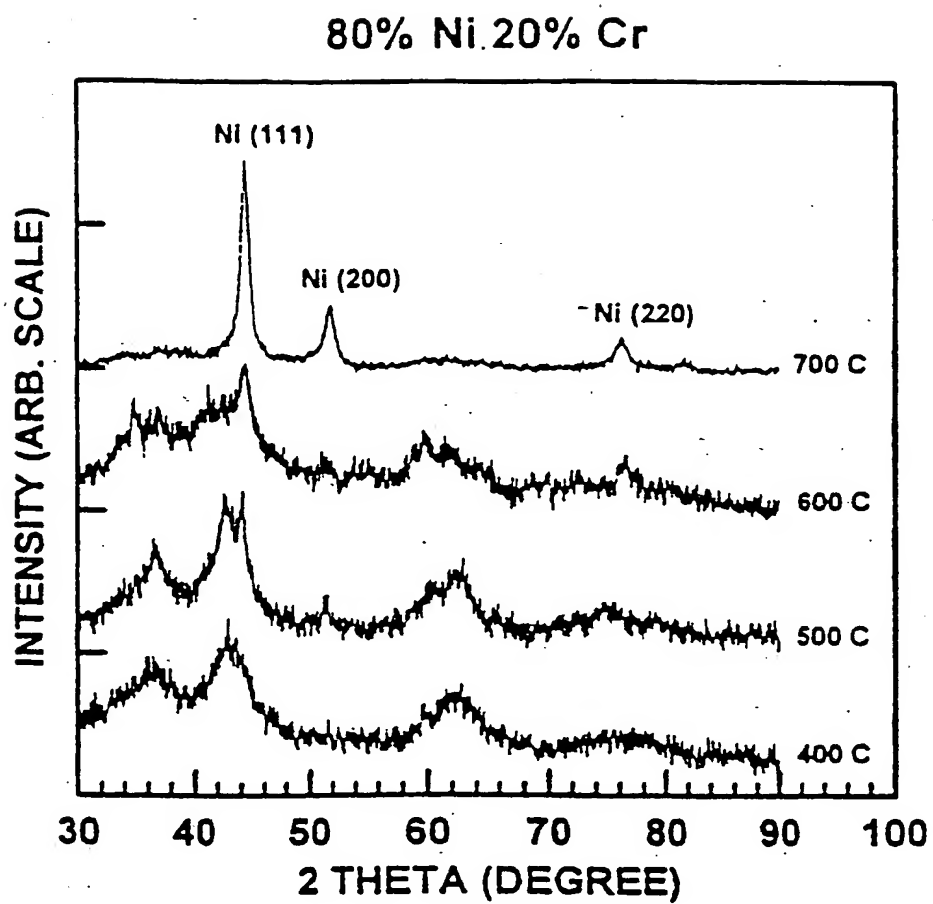


FIGURE 5

6/11

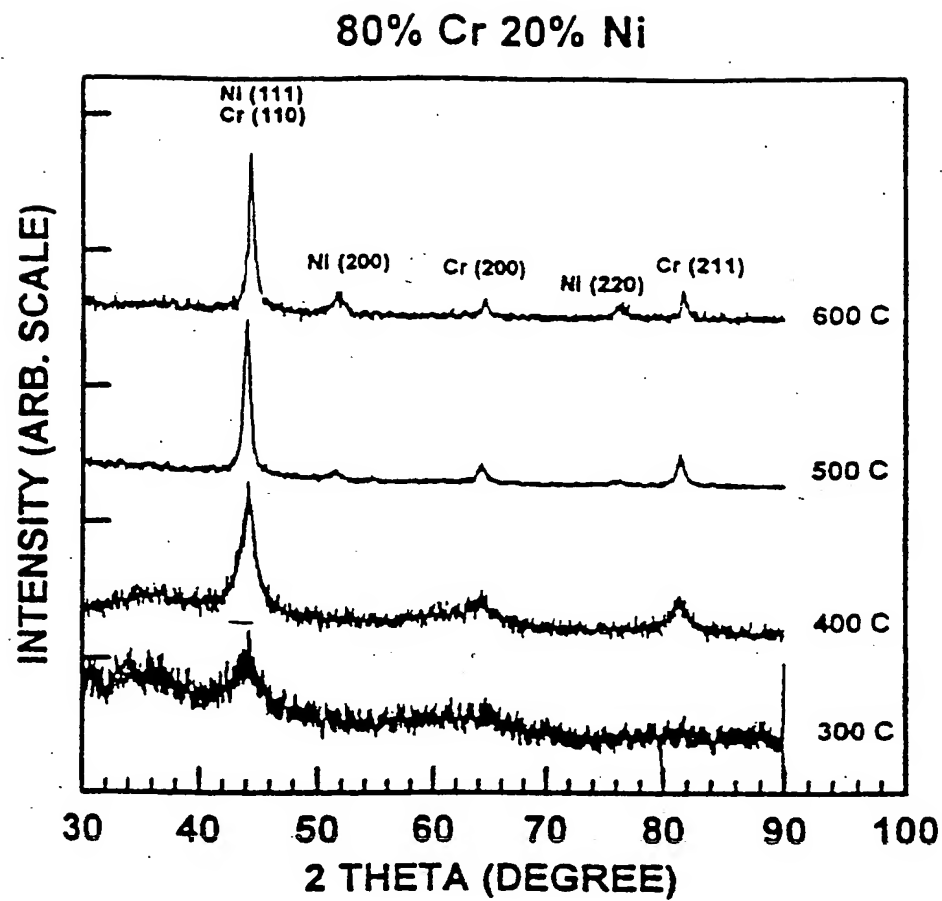


FIGURE 6

7/11

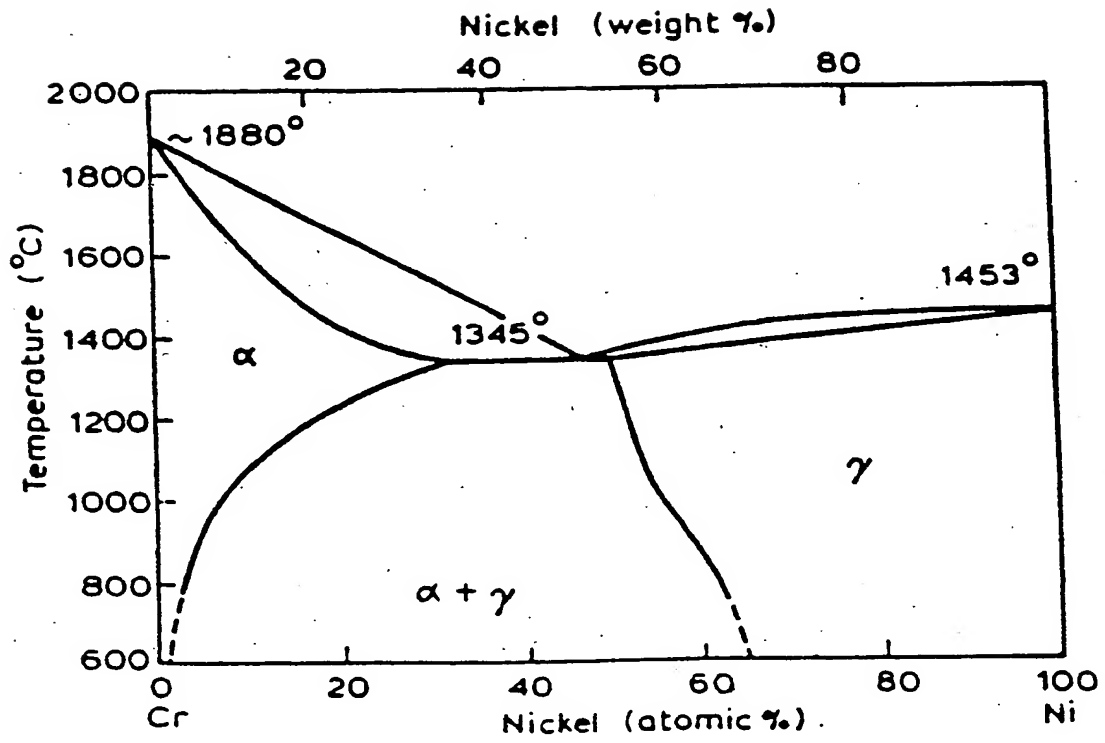


FIGURE 7

8/11

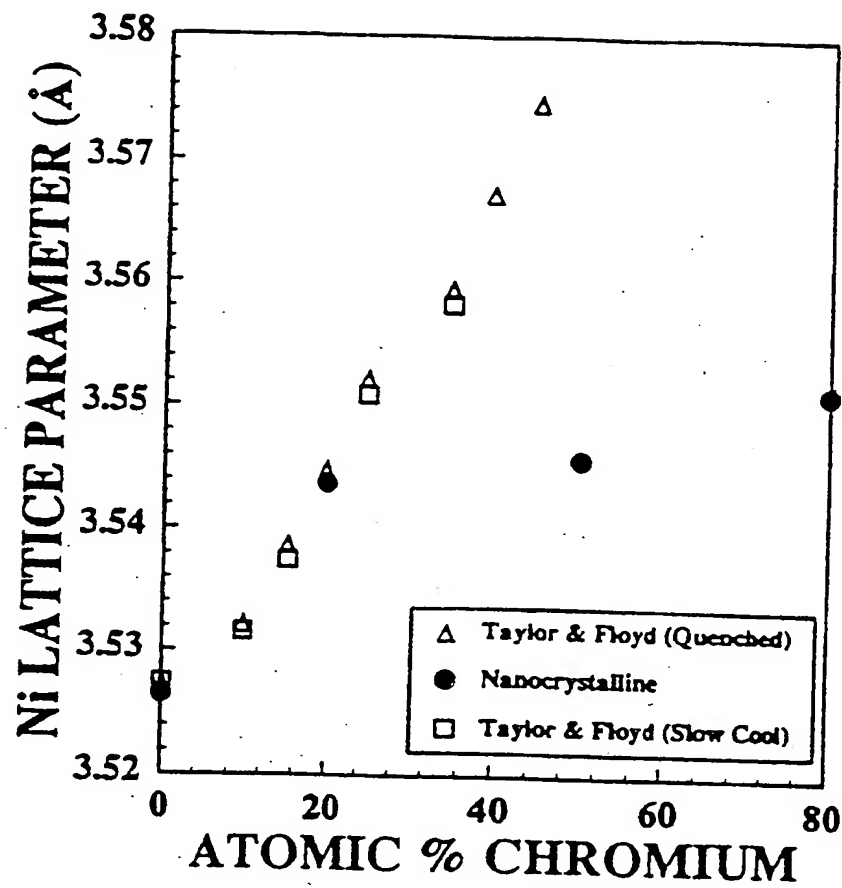


FIGURE 8

9/11

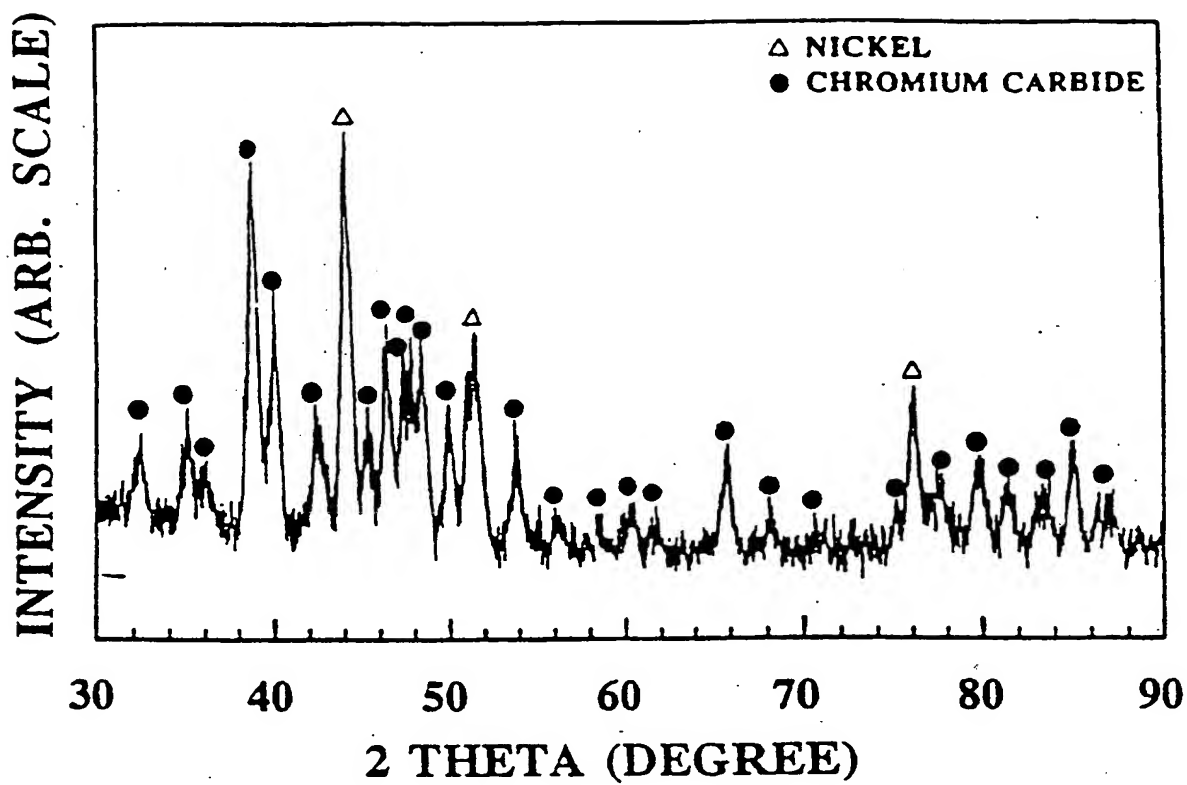


FIGURE 9

10/11

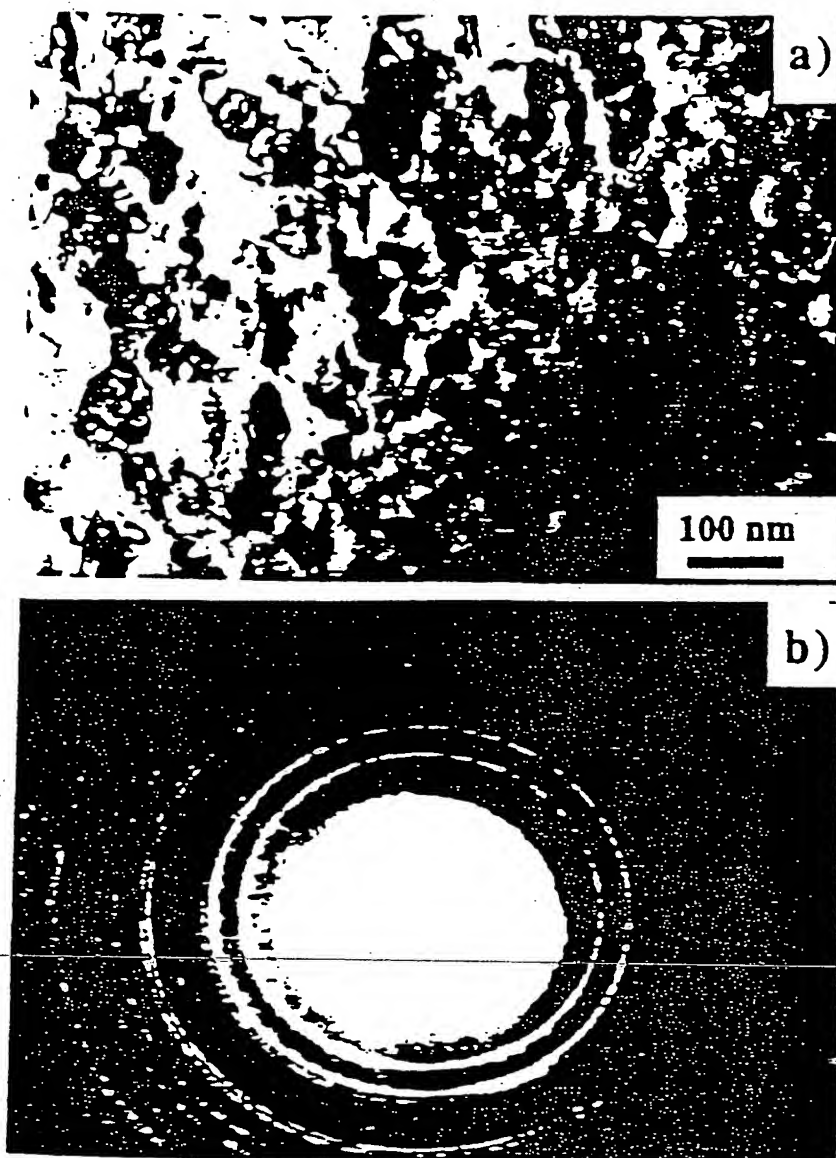


FIGURE 10

11/11

Histogram of Current Image  
Feature : Length  
Unit : nm  
Classes : 20  
Underflow: 0  
Overflow : 0

Frames : 1  
Objects : 292  
Max Cnt : 61  
Min Val : 3.2582  
Max Val : 94.277  
Tot Sum : 9834.2  
Mean : 33.679  
Std Dev : 10.178

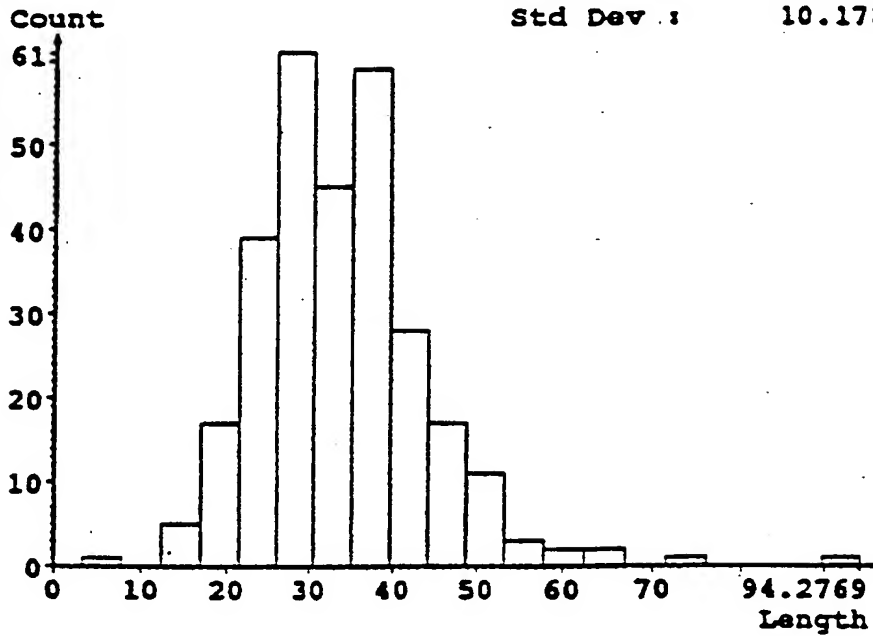


FIGURE 11

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/22614

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 B22F9/24 B22F1/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XIAO T D ET AL: "Synthesis of nanostructured Ni/Cr and Ni-Cr <sub>3</sub> C <sub>2</sub> powders by an organic solution reaction method" NANOSTRUCTURED MATERIALS, vol. 8, no. 7, November 1996, page 857-871 XP004015566 see paragraph 5; figure 9	1-27
X	ZENG D ET AL: "SYNTHESIS AND CHARACTERIZATION OF NANOPHASE GROUP 6 METAL (M) AND METAL CARBIDE (M <sub>2</sub> C) POWDERS BY CHEMICAL REDUCTION METHODS" CHEMISTRY OF MATERIALS, vol. 5, no. 5, 1 May 1993, pages 681-689, XP000372516 see page 688, right-hand column, line 30 - page 689, right-hand column, line 14	1-11, 14-19, 21-27
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 April 1998

Date of mailing of the international search report

21/04/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Schruers, H

# INTERNATIONAL SEARCH REPORT

Inter:      nal Application No

PCT/US 97/22614

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHOW G M ET AL: "CHEMICAL PRECIPITATION AND PROPERTIES OF NANOCRYSTALLINE FE-CU ALLOY AND COMPOSITE POWDERS" NANOSTRUCTURED MATERIALS, vol. 1, no. 5, 1 January 1992, pages 361-368, XP000342548 see page 368, line 3 - line 14 -----	1,2,5,6, 8-10,14, 16,17, 19,21, 23,24,26
X	EP 0 568 862 A (STARCK H C GMBH CO KG) 10 November 1993 see claim 1 -----	1-4
X	DE 42 14 719 A (STARCK H C GMBH CO KG) 11 November 1993 see column 2, line 53 - column 4, line 27 -----	1-4

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 97/22614

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0568862 A	10-11-93	DE 4214723 A AT 149109 T DE 59305507 D IL 105591 A JP 6073401 A US 5403375 A	11-11-93 15-03-97 03-04-97 12-09-96 15-03-94 04-04-95
DE 4214719 A	11-11-93	IL 105592 A JP 6049514 A SE 9301466 A US 5472477 A	05-12-96 22-02-94 05-11-93 05-12-95

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**